



Research article

Modeling and simulation of pervaporation (PV) separation for alcohol dehydration

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ABSTRACT

The separation performance of commercial crosslinked poly (vinyl alcohol) (PVA) membranes (i. e., the new commercial membrane PERVAP™ 4100 H F and standard membrane PERVAP™ 4100) used for the dehydration of two alcohol-water systems (i.e., ethanol-water and isopropanol-water mixtures, with an azeotropic point) were studied based on pervaporation process (PV) experimental data and mathematical modeling. Pervaporation process experiments proved that these two membranes have excellent applicability for the dehydration of alcohol. A semi-empirical solution-diffusion transport model was developed to describe the mass transport in the PVA membranes, which showed a good agreement with the experimental values. The universal quasi-chemical (UNIQUAC) model was utilized to predict the activity coefficient of nonideal alcohol-water systems in PVA membranes. In addition to the UNIQUAC model, the transport of alcohol-water across the commercial polymeric membrane was modeled using the conventional driving force model. The PV process experimental data with the mathematical model were used to develop the diffusivity correlations for water and alcohol (i.e., ethanol and isopropanol) through the PVA membranes. It was found that for swollen membranes (PVA), the developed correlations of water and alcohol diffusivity were strongly influenced by the feed water activity and feed temperature. Based on the mass transport model and developed diffusivity correlations, the permeation flux of water and alcohol through the PVA membranes was predicted, and the results showed a good agreement between the experimental data and the predictive model. The mean relative errors estimated for the permeate mass fluxes of water were 8.4%, and 3.8%, and for the permeate mass fluxes of ethanol were 18%, and 13.6% for the PERVAP™ 4100 and 4100 H F, respectively, as well as for the IPA-water-PVA system are as follows: 5% and 2.8% for the permeate mass fluxes of water and 14.4%, and 12.6% for the permeate mass fluxes of IPA for the PERVAP™ 4100 and 4100 H F, respectively.

1. Introduction

The pervaporation process (PV) is a membrane separation process that allows the desired components of a liquid feed to transport through the membrane by selective sorption and diffusion, which is followed by phase transition from the liquid phase to the vapor phase. The PV process has three main industrial applications: (1) dehydration of organic solvents, (2) removal of organic compounds (in trace amounts) from aqueous streams; and (3) separation of organic-organic solutions. The most important industrial application of

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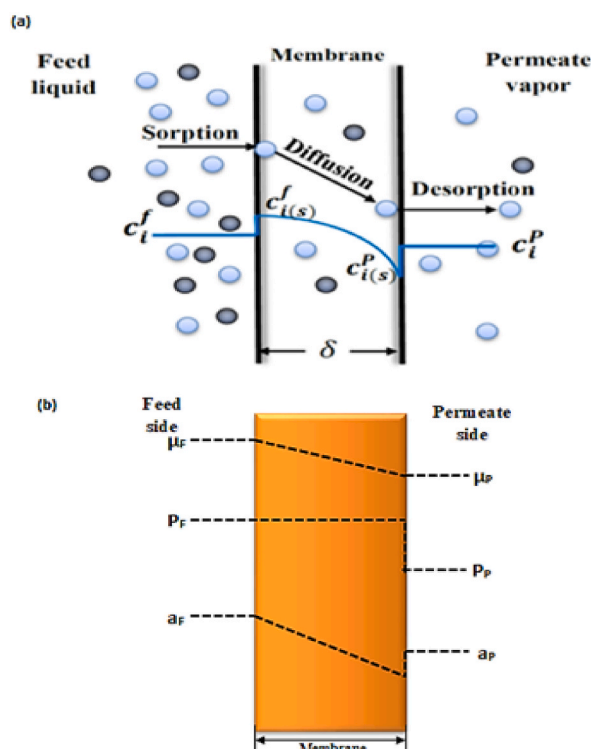


Fig. 1. (a) Schema of mass transfer in the solution-diffusion model [16], and (b) chemical potential, activity gradients, and pressure in the solution-diffusion model [26].

the PV process is the dehydration of organic solvents using hydrophilic membranes. The PV process is extensively used for alcohol dehydration (e.g., ethanol, isopropanol, t-butanol, and tetrahydrofuran) that forms an azeotropic mixture with water at a certain composition [1]. This process has been considered as an alternative to many conventional processes (e.g., extractive or azeotropic distillation) to separate azeotropic mixtures, mixtures with close boiling points, and mixtures of heat-sensitive compounds [2]. In the PV process, only a minor part of the mixture is selectively separated; therefore, this process requires low energy compared to distillation. One significant advantage of employing the PV process to separate azeotropic mixtures is that it can be accomplished without using entrainers that must be removed through additional separation steps, as in conventional separation techniques. In addition, the PV process can be combined with traditional separation processes, such as liquid-liquid extraction, distillation, absorption, chemical reactors, etc., where traditional separation techniques are insufficient.

The PV process scale-up requires a reliable mass transport model that can predict the PV membranes' performance under various operating conditions. It is essential to understand the mass transport mechanism through PV membranes to provide useful information for research to select suitable membrane materials and to develop appropriate membranes with high permeation flux as well as high separation efficiency. Generally, the development of accurate mass transport models can help to (1) reduce time-consuming experiments, (2) design better membrane materials, and (3) troubleshoot the PV process. The separation performance of the PV process is affected by a number of parameters, which can be classified into two main categories [3].

1. Process variables, such as feed concentration (feed composition, the nature of components, the interaction force between the components and the membrane), feed temperature, flow rate in the feed side, and pressure of the permeate side.
2. Intrinsic variables, such as the nature of the membrane materials (hydrophilic or hydrophobic), the membrane surface physical structure, degree of membrane cross-linking, and degree of membrane plasticization (swelling).

The interaction between permeants and the membrane is the limiting factor that determines membrane performance. Therefore, it is difficult to provide a comprehensive model to depict the transport behavior of nonideal systems (e.g., alcohol-water-PVA systems) in the PV process; this could be attributed to the complex chemical and physical interaction between permeated components and membrane material as well as to swelling effects [4]. In principle, two major approaches have been developed to describe the mass transport phenomena in the PV process: (1) the solution-diffusion (SD) model and (2) the pore flow model [5,6].

The solution-diffusion mechanism is the most accepted model to describe the mass transport mechanism through a dense polymeric membrane in the pervaporation process [7–12]. This model was first proposed by Graham in 1866 to describe gas permeability across rubber septa [13], and it has been widely used for the PV process by most researchers due to its good agreement with experimental results.

According to the solution-diffusion model, transport of components across the nonporous membrane consists of three consecutive, basic steps [14–17].

1. Preferential sorption of the permeating components from the liquid in the feed side to the membrane surface.
2. Diffusion of the permeating components across the membrane.
3. Desorption of the permeating components to the vapor phase on the permeate side of the membrane.

In this model, the feed components are first sorbed onto the membrane surface and then diffused through the membrane. In this model, the difference in the components' solubility and diffusivity through the membrane are the basis of separation [18]. Therefore, the selectivity and permeation rate are mainly controlled by the sorption and diffusion steps [19,20]. However, the desorption step in the permeate side is very fast due to the application of a vacuum or a sweeping gas and thus has little impact on the pervaporation transport compared to the sorption and diffusion steps [21–23].

The solution-diffusion (SD) model assumes that a thermodynamic equilibrium exists at the two sides of the membrane interface (i.e., feed and permeate sides). The SD model also assumes that the pressure across the membrane is constant and equal to the high-pressure value of the feed side. Therefore, there is a pressure step change at the membrane interface of the permeate side. According to this model, the driving force of the PV mass transfer is the chemical potential gradient for each component across the membrane, which is expressed only by the concentration gradient between the feed and permeate sides [24,25].

Fig. 1 (a, b) shows the transport mechanism of the solution-diffusion model with the effect of the chemical potential (μ), activity coefficient gradient (a), and pressure (p), across the membrane.

Solubility (sorption) is a thermodynamic parameter that is mainly determined by the chemical nature of the membrane material and the permeating molecules and provides a measure of the amount of penetrant that is sorbed by the membrane at equilibrium conditions. In contrast, diffusivity is a kinetic parameter that indicates how fast a penetrant is transported across the membrane, which is determined by the micro-morphology of the membrane structure and the size and shape of the penetrating molecules [27,28] as well as by the mutual interactions between the penetrant molecules and the membrane material [29].

The solution-diffusion model requires knowledge of the sorption and diffusion of various components through the membrane. Lipnizki and Trägårdh (2001) have reviewed different models to predict sorption and diffusion, which also predict the mass transfer across a selective dense layer. They categorized these models into three types, namely: (1) theoretical, (2) empirical, and (3) semi-empirical [30].

In this study a develop model was presented to prove that the exponential dependence of the diffusion coefficient on the feed water activity (preferred component) and membrane plasticization parameter and the plasticization parameter for a high swelling hydrophilic membrane is not constant and affected by both the feed water concentration and feed temperature which were not covered in the literature. The model was based on using the diffusivity correlation to develop a mass transfer model for predicting the mass transfer of water and alcohols through the selective separating layer during alcohol dehydration by the PV process. In this study, the UNIQUAC model was used to simulate the sorption equilibria of nonideal alcohol-water mixtures in highly hydrophilic membranes. The experimental PV data along with the solution-diffusion mass transport model were used to estimate the diffusion coefficient of water and alcohols through the PVA membranes and to predict semi-empirical diffusivity correlations as a function of the feed water activity and plasticization parameters. The model is validated by experimental results from the PV of alcohol/water mixture using the new commercial membrane PERVAP™ 4100 H F and standard membrane PERVAP™ 4100.

2. Experimental work of pervaporation process

The setup of the PV process for this study was described in our previous work and had an effective membrane area of 100.2 cm² [31]. The alcohol-water mixture was circulated across the membrane surface at a flow rate of 1.6 L/min. The feed water concentration was varied from 5 to 15 wt%, and from 7 to 18 wt%, and the pressure of the permeate side was maintained at 53 mbar and 26 mbar for EtOH-water mixtures and IPA-water mixtures, respectively. After reaching the steady state (1–1.5 h), the permeate samples were collected at regular time intervals using a cold trap kept in liquid nitrogen and were analyzed by a pre-calibrated Abbe refractometer (sensitivity 0.0001, Atago-3T, Japan). The feed temperature was adjusted to 60, 65, and 70 °C using a water bath. The mass of the permeate samples was weighed using a digital balance with an accuracy of 0.001 g. Although it is known that the initial water content in the feed mixture influence the plasticisation of the swollen membranes (PVA), and thus fluxes of the components through it [32]. In this study, the intermediate drying of the membranes (PERVAP™ 4100 and PERVAP™ 4100 H F) between experiments was not conducted because the initial water content in the feed mixture was low and did not cause swelling of the membranes.

3. Materials

Two commercial hydrophilic membranes (i.e., PERVAP™ 4100 and 4100 H F) from DeltaMem AG (Switzerland) were used. These composite membranes consist of poly (vinyl alcohol) (PVA) as a thin selective layer with a different degree of cross-linking and different thicknesses, cast on an asymmetric porous polyacrylonitrile (PAN) membrane as a support layer and coated onto a nonwoven fabric layer. The membrane characterization was described in our previous work [31].

Ethanol and isopropanol were purchased from Chem Lab NV, Zedelgem (Belgium) and Thommen-Furler AG (Switzerland). Distilled water was used to prepare the simulated alcohol-water mixtures.

4. Model assumptions

The solution-diffusion model is an acceptable model for describing the mass flux in polymeric membranes. In this model, measuring the sorption and diffusion of components across the membrane are two key steps in determining the rates of mass transfer and selectivity of the membrane. The assumptions used in the present model are outlined below.

1. The solution-diffusion theory holds true.
2. There is no reaction between species in the membrane.
3. The temperature is constant across the membrane.
4. The pressure is constant across the membrane and equal to the feed side pressure.
5. There is a thermodynamic equilibrium at the two side surfaces of the membrane in contact with the feed and permeate sides.
6. The system is steady state, and the penetration of components occurs in one dimension across the thickness of the membrane.
7. The resistance is negligible when transporting the penetrants on the feed side boundary layer and the microporous support layer.
8. The concentration of species on the permeate side of the membrane approaches zero under vacuum pressure on the permeate side (53 mbar for an ethanol-water mixture and 26 mbar for an isopropanol-water mixture).

5. Membrane sorption modeling

In the PV process, the sorption of species at the membrane-liquid interface occurs in a thermodynamic equilibrium between the polymer and the external fluid phase. Knowledge of the membrane’s ability to engage in the sorption of all species plays a critical role in predicting the pervaporation membrane separation performance [33]. The sorption strongly depends on the feed composition, feed temperature, the interaction between the permeates and membrane material, the mutual interaction between the penetrates, and the degree of membrane cross-linking. The components with the highest affinity to the membrane material will preferentially sorb into the membrane. Ideal sorption in the membrane can be expected when the mutual interactions between the penetrating components are weak and the sorption of the target component is not affected by the other components’ concentration in the feed. In the case of ideal sorption, the component concentration in the membrane interface at equilibrium is linearly proportional to the component concentration in the feed, which is expressed by Henry’s law. This is mainly observed for the sorption of gases in polymers. For a nonideal system, such as the PV process, the assumption of ideal sorption cannot be used because the interaction between the membrane material and penetrants is strong. Therefore, researchers have suggested various theories for predicting the sorption behavior of PV membranes toward multicomponent liquid mixtures, such as the Flory-Huggins model [34], Flory-Rehner model [35], UNIQUAC model [36], UNIQUAC functional-group activity coefficients (UNIFAC) model [37,38], etc., and also a combination of these models. All models are suitable and can be used to predict membrane sorption depending on the availability of the system interaction parameters. Therefore, in the absence of experimental data to obtain the system interaction parameters, the UNIQUAC or UNIFAC methods are suitable to predict membrane sorption since they only require parameters for the contributions of functional groups and the mutual interactions between the components in the mixture.

The UNIQUAC model has been widely used to predict the solubility of nonideal mixtures in a dense active layer. Abrams and Prausnitz (1975) proposed the UNIQUAC model to predict liquid-liquid and liquid-vapor equilibrium in binary and multicomponent systems, including polymers [36].

Heintz and Stephan (1992, 1994) predicted the sorption of nonideal systems with a dense selective layer (e.g., alcohol-water mixtures in the PVA membranes) using the UNIQUAC model. In the UNIQUAC model, the activity coefficient of component i (a_i) in a multicomponent system consists of two parts, a combinatorial portion (a_i^C) due to variations in the shape and size of the molecules that contribute to the entropy of mixing, and a residual portion (a_i^R) due to the interaction energies/enthalpy of mixing [39]. Therefore, the activity coefficient of component i (a_i) in a liquid multicomponent system (containing n components) can be expressed using Eq. (1):

$$\ln a_i = \ln a_i^C + \ln a_i^R \tag{1}$$

$$\ln a_i(\Phi_1, \dots, \Phi_n, \Phi_p) = \ln \Phi_i + \frac{z}{2} q_i \ln \left[\frac{\theta_i}{\Phi_i} \right] + l_i - \sum_{j=1}^n \Phi_j \frac{r_j}{r_i} l_j - r_i \Phi_p \left[\frac{z}{2} \left[1 - \frac{q_p}{r_p} \right] - 1 \right] - q_i^* \ln \sum_{j=1}^n \theta_j^* \tau_{ji} + q_i^* - q_i^* \sum_{j=1}^n \frac{\theta_j^* \tau_{ij}}{\sum_{k=1}^n \theta_k^* \tau_{kj}} \tag{2}$$

Where, the variables Φ_i , θ_i , θ_i^* , l_i (in Eq. (2)) can be calculated using equations (3)–(6).

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^n r_j x_j} \tag{3}$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^n q_j x_j} = \frac{\left[\frac{q_i}{r_i} \Phi_i \right]}{\sum_{j=1}^n \left[\frac{q_j}{r_j} \Phi_j \right]} \tag{4}$$

$$\theta_i^* = \frac{q_i^* x_i}{\sum_{j=1}^n q_i^* x_j} = \frac{\left[\frac{q_i^*}{r_i} \Phi_i \right]}{\sum_{j=1}^n \left[\frac{q_j^*}{r_j} \Phi_j \right]} \quad (5)$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1) \quad (6)$$

where x_i is the component mole fraction; n is the number of components in the mixture; θ and θ^* are the component surface fractions; φ is the component volume fraction; Z is the coordination number assumed to be 10; r , l , q , and q^* are parameters related to the molecule's geometry (shape and size); τ_{ij} and τ_{ji} are the binary intermolecular interaction parameters between the mixture components that can be estimated by fitting the above equation to the vapor-liquid equilibrium (VLE) data of the liquid mixture [40]. Additionally, the binary interaction parameters between the solvent and polymer material (τ_{ip} , τ_{pi}) can be obtained by fitting the vapor sorption experimental data of a pure component to Eq. (2) [40]. The last two terms (containing q^* and θ^*) were added to Eq. (2) to take into account the effect of the hydrogen bonding present in the system. Heintz and Stephan (1994) reported these data for an alcohol-water-PVA mixture [41].

The binary interaction parameters of the solvent-polymer material as well as the solvent-solvent interaction parameters (in Eq. (2)) can be expressed as a function of the feed temperature, as shown in Eqs. (7) and (8):

$$\tau_{ij} = \exp\left(\frac{-u_{ij}}{RT}\right), \text{ for polymer - solvent interaction parameter} \quad (7)$$

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T}\right), \text{ for solvent - solvent interaction parameters} \quad (8)$$

The parameters a_{ij} , and b_{ij} , can be found in the database of ASPEN PLUS.

6. Permeation flux through the membrane

The continuity equation for the transport of component i across the membrane can be expressed as the following equation:

$$\rho_i \left(\frac{d\Phi_i}{dt} + u \nabla \Phi_i \right) = \nabla(-J_i) + R_a, \text{ for } i = 1, 2 \quad (9)$$

where ρ is density, u is the fluid velocity (m/s), J_i is the flux of the mass transfer, t is the time in seconds (s), Φ_i is the component volume fraction, and R_a is the rate of reaction (mol/m³. s).

Diffusion is the predominant phenomenon for mass transport inside the membrane, and the mass transport by convection is negligible. Therefore, at steady state, the continuity equation (Eq. (9)) for the component i transport across the membrane can be written as follows:

$$\nabla(-J_i) = 0 \quad (10)$$

For a hydrophilic polymeric membrane, the mass transfer flux of component i can be expressed as

$$J_i = -C_i L_i \frac{d\mu_i}{dz} \quad (11)$$

The chemical potential for the isothermal process can be estimated from

$$\mu_i = \mu_i^o + RT \ln a_i + V_i P \quad (12)$$

The derivative of the chemical potential (Eq. (12)) is written as

$$d\mu_i = RT d \ln a_i + V_i dP \quad (13)$$

where V_i is the molar volume, P is the pressure of the system, and a_i is the activity of component i . According to the solution-diffusion model, the pressure is constant through the membrane. Therefore, Eq. (13) is written as

$$d\mu_i = RT d \ln a_i \quad (14)$$

Substituting Eq. (14) into Eq. (11), the permeation flux of component i can be written as

$$J_i = -C_i L_i RT \frac{d \ln a_i}{dz} \quad (15)$$

The thermodynamic diffusivity (D_{iT}) of component i through the polymeric membrane can be expressed using Eq. (16):

$$D_{iT} = L_i RT \quad (16)$$

C_i is the concentration of component i that can be related to the volume fraction according to the following relation:

$$C_i = \rho_i \Phi_i \tag{17}$$

Substituting Eqs. (16) and (17) into Eq. (15) produces the following equation:

$$J_i = -D_{iT} \Phi_i \rho_i \frac{dlna_i}{dz} \tag{18}$$

For the ternary system (binary mixture-membrane), the coupling of fluxes is assumed. Therefore, the activity of component i (a_i) will depend on the volume fraction (Φ) of all components (i and j) in the polymeric membrane. Hence, Eq. (18) can be written as follows:

$$J_i = -D_{iT} \Phi_i \rho_i \left[\frac{dlna_i}{d\Phi_i} \frac{d\Phi_i}{dz} + \frac{dlna_j}{d\Phi_j} \frac{d\Phi_j}{dz} \right] \tag{19}$$

$$J_j = -D_{jT} \Phi_j \rho_j \left[\frac{dlna_j}{d\Phi_j} \frac{d\Phi_j}{dz} + \frac{dlna_i}{d\Phi_i} \frac{d\Phi_i}{dz} \right] \tag{20}$$

According to Eqs. (19) and (20), the permeation flux of component i depends on its concentration gradient and the concentration gradient of all other components in the polymeric membrane matrix. Knowledge of the sorption equilibrium, boundary conditions, and diffusivities is essential for computing the permeation flux of each component across the polymeric membrane.

Substituting Eqs. (19) and (20) into Eq. (10) produces the following differential equations (Eqs. (21) and (22)):

$$\nabla \left(D_{iT} \Phi_i \rho_i \left[\frac{dlna_i}{d\Phi_i} \frac{d\Phi_i}{dz} + \frac{dlna_j}{d\Phi_j} \frac{d\Phi_j}{dz} \right] \right) = 0 \tag{21}$$

$$\nabla \left(D_{jT} \Phi_j \rho_j \left[\frac{dlna_j}{d\Phi_j} \frac{d\Phi_j}{dz} + \frac{dlna_i}{d\Phi_i} \frac{d\Phi_i}{dz} \right] \right) = 0 \tag{22}$$

For a ternary system (binary mixture-membrane), Eq. (2) can be written as

$$\ln a_i(\Phi_1, \Phi_2, \Phi_p) = \ln \Phi_i + \frac{z}{2} q_i \ln \left[\frac{\theta_i}{\Phi_i} \right] + l_i - \sum_{j=1}^n \Phi_j \frac{r_{ij}}{r_j} - r_i \Phi_p \left[\frac{z}{2} \left[1 - \frac{q_p}{r_p} \right] - 1 \right] - q_i^* \ln \sum_{j=1}^n \theta_j^* \tau_{ji} + q_i^* - q_i^* \frac{\sum_{j=1}^n \theta_j^* \tau_{ij}}{\sum_{k=1}^n \theta_k^* \tau_{kj}} \tag{23}$$

By differentiating Eq. (23) with respect to the component volume fractions Φ_i and Φ_j, the partial derivative of the activity can be written as

$$\frac{dlna_i}{d\Phi_i} = \frac{1}{\Phi_i} + \frac{z}{2} q_i \frac{\Phi_i}{\theta_i} \frac{d}{d\Phi_i} \left[\frac{\theta_i}{\Phi_i} \right] - l_i + r_i \left[\frac{z}{2} \left(1 - \frac{q_p}{r_p} \right) - 1 \right] - \frac{q_i^*}{\sum_{j=1}^n \theta_j^* \tau_{ji}} \left[\sum_{j=1}^m \left(\tau_{ji} \frac{d\theta_j^*}{d\Phi_i} \right) \right] - q_i^* \frac{\sum_{k=1}^m \theta_k^* \tau_{kj} \left(\frac{d\theta_j^*}{d\Phi_i} \tau_{ij} \right) - \left(\theta_j^* \tau_{ij} \right) \left(\sum_{k=1}^m \tau_{kj} \frac{d\theta_k^*}{d\Phi_i} \right)}{\left(\sum_{k=1}^m \theta_k^* \tau_{kj} \right)^2} \tag{24}$$

$$\frac{dlna_i}{d\Phi_j} = \frac{z}{2} q_i \frac{\Phi_i}{\theta_i} \frac{d}{d\Phi_j} \left[\frac{\theta_i}{\Phi_i} \right] - \frac{r_{ij}}{r_j} l_i + r_i \left[\frac{z}{2} \left(1 - \frac{q_p}{r_p} \right) - 1 \right] - \frac{q_i^*}{\sum_{j=1}^n \theta_j^* \tau_{ji}} \left[\sum_{j=1}^m \left(\tau_{ji} \frac{d\theta_j^*}{d\Phi_j} \right) \right] - q_i^* \frac{\sum_{k=1}^m \theta_k^* \tau_{kj} \left(\frac{d\theta_j^*}{d\Phi_j} \tau_{ij} \right) - \left(\theta_j^* \tau_{ij} \right) \left(\sum_{k=1}^m \tau_{kj} \frac{d\theta_k^*}{d\Phi_j} \right)}{\left(\sum_{k=1}^m \theta_k^* \tau_{kj} \right)^2}, \text{ for } i \neq j \tag{25}$$

The partial derivatives in Eqs. (24) and (25) are defined as

$$\frac{d}{d\Phi_k} \left(\frac{\theta_i}{\Phi_i} \right) = \frac{-\left(\frac{q_i}{r_i} \right) \sum_{j=1}^m \left[\frac{d}{d\Phi_k} \left(\frac{q_j}{r_j} \Phi_j \right) \right]}{\left[\sum_{j=1}^n \Phi_j \left(\frac{q_j}{r_j} \right) \right]^2}, \text{ for all } i \text{ and } k \tag{26}$$

$$\frac{d\theta_i}{d\Phi_k} = \frac{\left[\sum_{j=1}^m \Phi_j \left(\frac{q_j}{r_j} \right) \right] \left(\frac{q_i}{r_i} \right) \frac{d\Phi_i}{d\Phi_k} - \left(\frac{q_i \Phi_i}{r_i} \right) \sum_{j=1}^m \left[\frac{d}{d\Phi_k} \left(\frac{q_j}{r_j} \Phi_j \right) \right]}{\left[\sum_{j=1}^m \Phi_j \left(\frac{q_j}{r_j} \right) \right]^2}, \text{ for all } i \text{ and } k \tag{27}$$

$$\frac{d\theta_i}{d\Phi_k} = \frac{\left[\sum_{j=1}^m \Phi_j \left(\frac{q_j^*}{r_j} \right) \right] \left(\frac{q_i^*}{r_i} \frac{d\Phi_i}{d\Phi_k} - \left(\frac{q_i^* \Phi_i}{r_i} \right) \sum_{j=1}^m \left[\frac{d}{d\Phi_k} \left(\frac{q_j^*}{r_j} \Phi_j \right) \right] \right)}{\left[\sum_{j=1}^m \Phi_j \left(\frac{q_j^*}{r_j} \right) \right]^2}, \text{ for all } i \text{ and } k \quad (28)$$

The above Eqs. (23)–(28) can be simplified further by using Eq. (29):

$$\Phi_p = 1 - (\Phi_i + \Phi_j) \quad (29)$$

The solution-diffusion model assumes that thermodynamic equilibrium exists at both the feed-membrane interface and the permeate-membrane interface, which indicates that the chemical potential that can be expressed by the activity of each component in the feed is equal to that in the membrane at the feed-membrane interface and also that the activity for each component in the permeate is equal to that in the membrane at the permeate-membrane interface. Therefore, the volume fraction of the components at both sides of the membrane can be estimated using the following mathematical expression:

$$a_{i,f} = a_{i,m,f} \text{ for all } i \quad (30)$$

$$a_{i,p} = a_{i,m,p} \text{ for all } i \quad (31)$$

where $a_{i,f}$ is the activity of component i in the liquid feed mixture and can be computed using the UNIQUAC theory. On the other hand, $a_{i,p}$ is the activity of component i in the permeate and can be computed by the ratio of the partial pressure of component i in the permeate side to the vapor pressure at the feed temperature ($P_i/P_{i,sat}$). The $a_{i,m,f}$ and $a_{i,m,p}$ in Eqs. (30) and (31) represent the activity of component i at the membrane phase, respectively, and can be substituted in Eq. (23) to solve the set of nonlinear algebraic equations using MATLAB's "fsolve" function to obtain the component volume fraction in the membrane at both the feed and permeate sides.

7. Diffusivity correlations

In PV separation processes, the diffusion coefficient is of paramount importance in the study of component behavior and mass transfer through membranes, and it is considered a rate-controlled step in the PV process. The diffusion coefficient is commonly affected by many factors, such as the coupling between diffusing components, component concentration, structure of the polymer, size of the permeating component, and degree of membrane swelling. Several fundamental models and semiempirical models have been suggested to predict and describe the diffusivity of components across the membrane.

Fujita (1961) developed the free volume theory to describe mass transport across polymeric membranes based on the fundamental assumption that the transport of solvent molecules across the membrane depends on the free volume available in the membrane structure [42]. According to this theory, the diffusivity of the permeant can be expressed as an exponential function of the polymer fractional free volume and two adjustable parameters that represent the interactions between the permeants and the polymer [42–44]. Yeom and Huang (1992) extended Fujita's free volume model from a binary to a ternary system. This model takes into account the coupling effect of the fluxes through the membrane and has been applied successfully to predict the permeation flux of ethanol-water mixtures in the cross-linked PVA membranes [45]. Later, Kim et al. (1995) applied this model to analyze the transport mechanism of ethanol-water mixtures through polyacrylonitrile (PAN) and other four other copolymers [46]. Vrentas and Duda (1977a, 1977b) extended the free volume theory to characterize the diffusivity of solvents in amorphous polymers and to explain the dependence of the diffusion coefficient on the concentration and temperature in the polymeric membrane [47,48].

Although the free volume theory has a satisfactory theoretical basis and has succeeded in explaining diffusion data for simple molecules, this theory has not gained much acceptance because it is insufficient to explain the diffusion of components through highly swollen membranes and also requires extensive experimental work to obtain the free volume parameters needed for this model. Because of these limitations, it is more common to use semiempirical correlations to describe the diffusivity of components across the polymeric membrane.

Several semiempirical diffusion-concentration relations have been proposed to describe and predict *trans*-membrane diffusion. For glassy polymers, Greenlaw et al. (1977) proposed that the diffusion coefficient is linearly dependent on the concentration of the permeating species [49]. In contrast, for rubbery polymers, Aptel et al. (1974) long model is used to explain the penetration of pure components through dense membranes; it assumes an exponential dependence of the diffusion coefficient on the component concentration [50]. This model has been replaced by the more popular "six coefficients model" proposed by Brun et al. (1985), which has been used to predict the diffusion coefficient for complex nonideal ternary systems [51]. The empirical parameters (called "softeners") in these models take into account the species' plasticizing effect on the polymeric membrane matrix and are assumed to be constant. This assumption is invalid for highly swollen membranes. In 2001, Shah assumed that the plasticization parameter is a function of the feed temperature [52]. Later, Valentinyi et al. (2013) assumed that this parameter is dependent on the feed concentration [53]. In this work, we have assumed that in the case of membranes that suffer from high swelling (e.g., PVA hydrophilic membranes), the plasticization parameter of the membrane is influenced by the temperature and concentration of the feed.

The diffusivity values of water, ethanol, and isopropanol in the ethanol-water system and IPA-water system were estimated for various feed temperatures and feed concentrations based on the values of the permeation flux obtained from the PV experiments and the proposed model for highly hydrophilic polymeric membranes; this model was described above to develop semiempirical diffusion

Table 1
UNIQUAC parameters for alcohol-water-PVA systems.

Solvent	a_{ij}	b_{ij} [K]	a_{ji}	b_{ji} [k]	u_{sp}/R [K]	u_{ps}/R [K]	r	q	q^*
Ethanol	-2.49	756.9	2.0	-728.9	632	230.9	2.11	1.97	0.92
Isopropanol	0	124.2	0	79.2	1072.4	318	2.78	2.51	0.89
Water	-	-	-	-	539.5	-366	0.92	1.47	1

$i = \text{water}$, $j = \text{alcohol}$, $s = \text{solvent}$, $p = \text{polymeric membrane}$; $q^*/r^* = 0.434$, and $q/r = 0.934$ for PVA polymer.

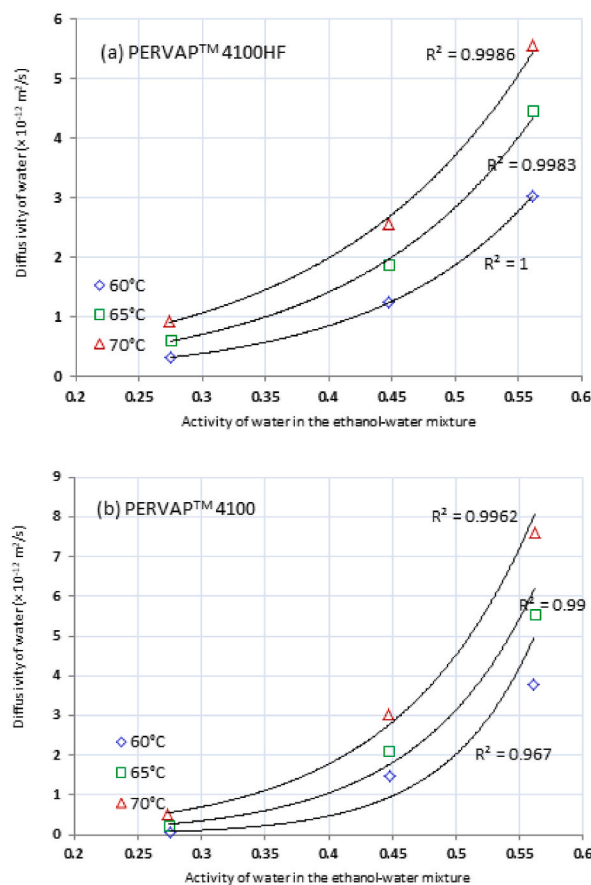


Fig. 2. Diffusivity of water through (a) PERVAP™ 4100 H F and (b) PERVAP™ 4100 membranes with the feed water activity for EtOH-water systems at different temperatures.

coefficient correlations dependent on these variables to predict the component permeation flux in the membrane. All parameters used as input to the model are shown in Table 1.

Fig. 2 (a, b) shows the variation in the water diffusivity across the PERVAP™ 4100 and 4100 HF membranes with the activity of the feed water at different temperatures for EtOH-water systems. The diffusion of water across both membranes rose with an increase in the feed water activity. This can be attributed to the plasticization effect on the membrane due to the increase in the free volume between the polymer chains, which facilitates the diffusion of the molecules through the membrane matrix. The diffusivity of the water at 65 °C increased from 2.4402×10^{-13} to 5.5502×10^{-12} m²/s for the PERVAP™ 4100 membrane and from 6.0254×10^{-13} to 4.4812×10^{-12} m²/s for the PERVAP™ 4100 HF membrane when the water activity in the feed increased from 0.2753 (5 wt% water) to 0.5611 (15 wt% water). The diffusivity of water (in trace amounts) in ethanol can be calculated using the Wilk-Chang correlation [54]. Using this correlation, the diffusivity of water in ethanol at 65 °C was calculated to be 3.2849×10^{-9} m²/s, which is higher than the water diffusivity through the PVA membranes by about three orders of magnitude. Additionally, the dependence of the water diffusivity across the membrane on the feed water activity tended to be exponential at all temperatures.

Based on the pervaporation experimental data, the plasticization of the hydrophilic membrane was influenced both by the water concentration in the feed solution and the feed temperature. Therefore, the correlation for estimating the plasticization parameter was a function of the feed temperatures and feed water concentration. Thus, the water diffusivity dependence for ethanol-water mixtures through cross-linked PVA membranes (i.e., PERVAP™ 4100 and 4100 H F) can be expressed as follows:

Table 2
Values of the estimated plasticization parameters for alcohol-water systems.

Ethanol-water/4100 H F	A1	A2	A3	A4	A5	A6	R ²
$\beta_1 = A_1 \times 12 T + A_2 \times 1 T + A_3 T + A_4 x_{12} + A_5 x_1 + A_6$	8.2344	-4.9894	0.8639	-2785.8	1690.3	-286.46	0.9964
$\beta_2 = A_1 \times 12 T + A_2 \times 1 T + A_3 T + A_4 x_{12} + A_5 x_1 + A_6$	28.947	-16.236	2.5084	-9767.1	5488.3	-834.69	0.9766
Ethanol-water/4100							
$\beta_1 = A_1 \times 12 T + A_2 \times 1 T + A_3 T + A_4 x_{12} + A_5 x_1 + A_6$	29.676	-16.239	2.3037	-10153	5548.9	-775.13	0.9994
$\beta_2 = A_1 \times 12 T + A_2 \times 1 T + A_3 T + A_4 x_{12} + A_5 x_1 + A_6$	61.83	-33.728	4.769	-21081	11,500	-1607.4	0.991
IPA-water/4100 H F							
$\beta_1 = A_1 \times 12 T + A_2 \times 1 T + A_3 T + A_4 x_{12} + A_5 x_1 + A_6$	15.847	-12.379	2.5361	-5356.1	4175.6	-845.37	0.9985
$\beta_2 = A_1 \times 12 T + A_2 \times 1 T + A_3 T + A_4 x_{12} + A_5 x_1 + A_6$	19.447	-15.382	3.3198	-6383.8	5083.8	-1090.4	0.9927
IPA-water/4100							
$\beta_1 = A_1 x_1^2 T + A_2 x_1 T + A_3 T + A_4 x_1^2 + A_5 x_1 + A_6$	15.967	-12.659	2.6302	-5571.6	4385.3	-890.47	0.9995
$\beta_2 = A_1 x_1^2 T + A_2 x_1 T + A_3 T + A_4 x_1^2 + A_5 x_1 + A_6$	27.82	-21.97	4.5911	-9598.4	7549.2	-1552.6	0.9628

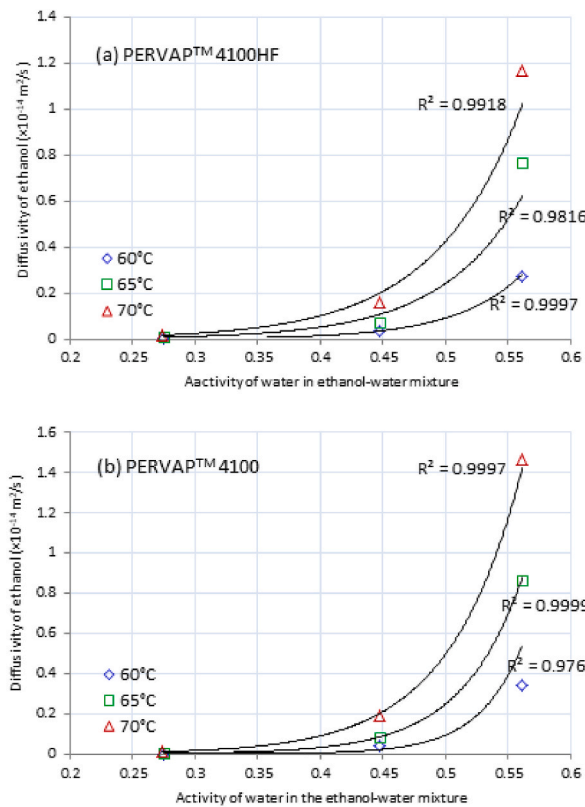


Fig. 3. Diffusivity of EtOH through (a) PERVAP™ 4100 H F and (b) PERVAP™ 4100 membranes with the feed water activity for EtOH-water systems at different temperatures.

$$D_w = 1.1 \times 10^{-13} e^{\beta_w a_{w,f}} \text{ for PERVAPTM 4100HF} \tag{32}$$

$$D_w = 1.7 \times 10^{-14} e^{\beta_w a_{w,f}} \text{ for PERVAPTM 4100} \tag{33}$$

Where β_w is the plasticization parameter and can be expressed using Eq. (34).

$$\beta_w = A_1 x_1^2 T + A_2 x_1 T + A_3 T + A_4 x_1^2 + A_5 x_1 + A_6 \tag{34}$$

where x_1 is the water mole fraction in the feed; and $A_1, A_2, A_3, A_4, A_5,$ and A_6 are the parameters for the water component that can be determined by fitting the diffusivity equations (32) and (33) to the experimental values of the diffusivity coefficient data points. The values of the estimated parameters are presented in Table 2.

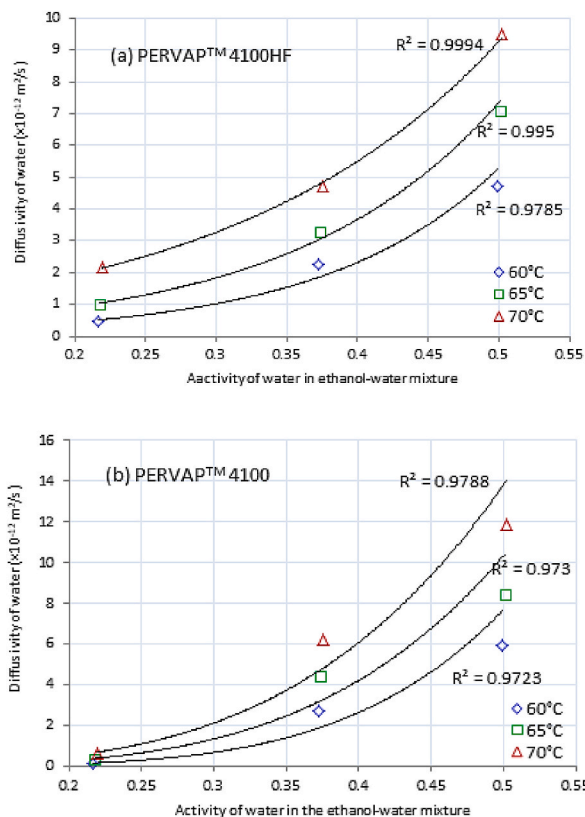


Fig. 4. Diffusivity of water through (a) PERVAP™ 4100 H F and (b) PERVAP™ 4100 membranes with the feed water activity for IPA-water systems at different temperatures.

Fig. 3 (a, b) shows the effect of the activity of the feed water on the diffusivity of ethanol through the PERVAP™ 4100 and 4100 H F membranes at different temperatures. Ethanol diffusivity at 65 °C increased from 2.30×10^{-17} to $8.63 \times 10^{-15} \text{ m}^2/\text{s}$ for the PERVAP™ 4100 membrane and from 8.5369×10^{-17} to $7.6793 \times 10^{-15} \text{ m}^2/\text{s}$ for the PERVAP™ 4100 H F membrane when the activity of the feed water increased from 0.2753 (5 wt% water) to 0.5611 (15 wt% water). Using the Wilk-Chang correlation, the diffusivity of the trace ethanol in bulk water at 65 °C was calculated to be $2.9209 \times 10^{-9} \text{ m}^2/\text{s}$, which is higher than the diffusivity of ethanol through the PVA membranes by about six orders of magnitude. In addition, the diffusivity of ethanol through the membranes was three times less than the diffusivity of water. This confirms the hydrophilic nature and the high separation performance of the membranes. It was also found that the ethanol diffusivity across the membrane increased exponentially with the activity of the feed water at all temperatures. This is due to the fact that for hydrophilic PVA membranes, the diffusivity of the organic components strongly depends on the plasticizing component activity (water), which causes membrane swelling and also depends on the effect of couplings between water and the organic component. The ethanol diffusivity dependence on the feed water activity can be expressed as

$$D_e = 1.36 \times 10^{-18} e^{\beta_e a_{w,f}} \text{ for PERVAP™ 4100HF} \tag{35}$$

$$D_e = 3.27 \times 10^{-19} e^{\beta_e a_{w,f}} \text{ for PERVAP™ 4100} \tag{36}$$

The plasticizing parameter for ethanol diffusivity through the membranes also depends on the feed water concentration and feed temperature, which can be calculated using Eq. (37):

$$\beta_e = A_1 x_1^2 T + A_2 x_1 T + A_3 T + A_4 x_1^2 + A_5 x_1 + A_6 \tag{37}$$

where $A_1, A_2, A_3, A_4, A_5,$ and A_6 are the parameters for the ethanol component that can be determined by fitting the diffusivity equations (35) and (36) to the experimental values of the diffusivity coefficients data points. The values of the estimated parameters are presented in Table 2.

Fig. 4 (a, b) shows the water diffusivity variation through the PERVAP™ 4100 and 4100 H F membranes with the feed water activity at different temperatures for IPA-water mixtures. The water diffusivity across the active layer of both membranes rose with increasing feed water activity. This behavior is similar to the behavior of water diffusivity for the EtOH-water mixture, as shown in Fig. 2 (a, b). The water diffusivity at 65 °C increased from 3.2170×10^{-13} to $8.4162 \times 10^{-12} \text{ m}^2/\text{s}$ for the PERVAP™ 4100 membrane and from 1.0019×10^{-12} to $7.0730 \times 10^{-12} \text{ m}^2/\text{s}$ for the PERVAP™ 4100 H F membrane when the water activity in the feed increased

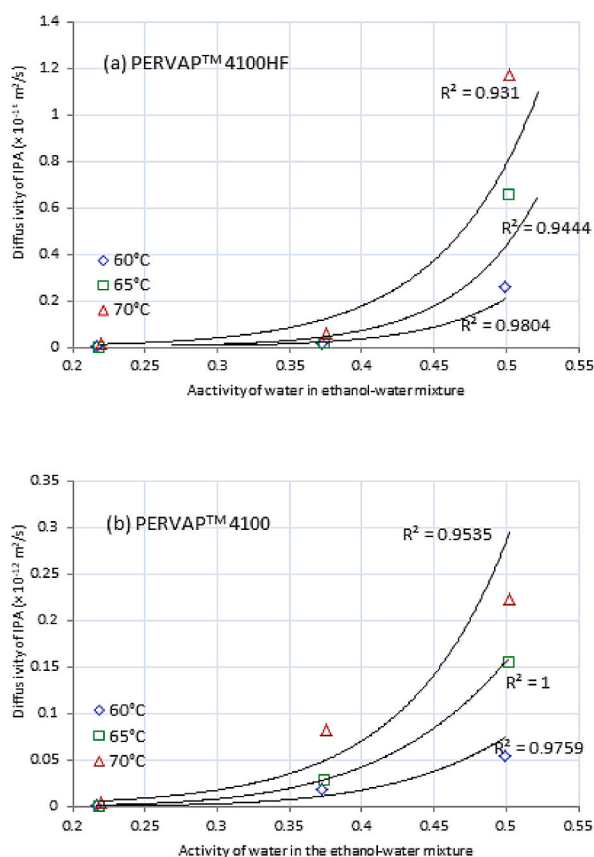


Fig. 5. Diffusivity of IPA through (a) PERVAP™ 4100 H F and (b) PERVAP™ 4100 membranes with the feed water activity for IPA-water systems at different temperatures.

from 0.2179 (7 wt% water) to 0.5008 (18 wt% water). Using the Wilk-Chang correlation, the water diffusivity in the IPA at 65 °C was calculated to be $2.10 \times 10^{-9} \text{ m}^2/\text{s}$, which is higher than the water diffusivity through the PVA membranes by three orders of magnitude. The values of the water diffusivity through the PVA membranes for the IPA-water mixtures were not very different from those of the ethanol-water mixtures. This indicates that feed water concentration has an actual effect on the water diffusivity behavior through hydrophilic PVA membranes. Therefore, the water diffusivity through both membranes (i.e., PERVAP™ 4100 H F and 4100) exhibited an exponential behavior similar to that of EtOH-water mixtures, following the same equations (32) and (33). The water plasticization parameter for the IPA-water mixtures also depended on the water concentration in the feed solution and feed temperature, as shown in Eq. (34).

Fig. 5 (a, b) shows the effect of the feed water activity on the diffusivity of the IPA through the PERVAP™ 4100 and 4100 H F membranes at different temperatures. The IPA diffusivity at 65 °C rose from 1.17×10^{-17} to $1.56 \times 10^{-15} \text{ m}^2/\text{s}$ for the PERVAP™ 4100 membrane and from 3.66×10^{-17} to $6.61 \times 10^{-15} \text{ m}^2/\text{s}$ for the PERVAP™ 4100 H F membrane when the activity of the feed water increased from 0.2179 (7 wt% water) to 0.5008 (18 wt% water). Using the Wilk-Chang correlation, the diffusivity of the trace IPA in bulk water at 65 °C was calculated to be $1.65 \times 10^{-9} \text{ m}^2/\text{s}$, which was higher than the diffusivity of the IPA through the PVA membranes by about six orders of magnitude. Thus, at high feed water activity, the isopropanol diffusivity through the PVA membranes remained low despite the swelling of the PVA selective layer due to the large kinetic diameter of isopropanol and the higher hydrophobicity that hinders its transport through the PVA membranes. As a result, these membranes can exhibit high selectivity to isopropanol-water mixtures at high feed water concentrations. It was also found that the IPA diffusivity across the membrane increased exponentially with the activity of the feed water, as in the case of an ethanol-water mixture, which strongly depends on the plasticizing component activity (water) and the effect of couplings between the water and isopropanol. Therefore, the IPA's diffusivity through both membranes (i.e., PERVAP™ 4100 and 4100 H F) is based on the same equations (35) and (36), and the IPA's plasticization parameter for the IPA-water mixtures also depended on the feed temperature and water concentration in the feed solution, as shown in Eq. (37).

8. Comparison of the predicted results with the experimental data

The comparison between the partial flux calculated by the predictive model and the experimental data for ethanol-water-PVA

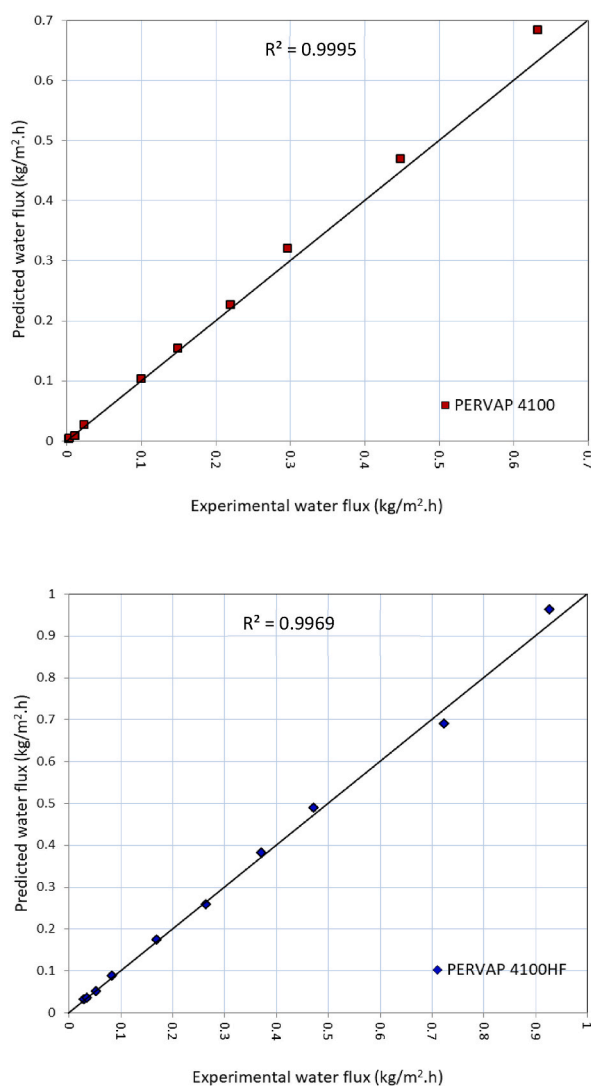


Fig. 6. Comparison of the experimental and predicted mass fluxes of water ($\text{kg}/\text{m}^2\text{h}$) in the ethanol-water systems for a) PERVAP™ 4100 and b) PERVAP™ 4100 H F membranes.

systems is shown in Fig. 6 (a, b) and Fig. 7 (a, b). Similar comparisons for the IPA-water-PVA systems are shown in Fig. 8 (a, b) and Fig. 9 (a, b) for the membranes PERVAP™ 4100 and 4100 H F, respectively.

Fig. 6 (a, b) and 7 (a, b) demonstrate that the proposed model properly predicts the influence of the feed composition and operating temperature on the partial fluxes because the mass fluxes calculated are in good agreement with the measured ones. The highest relative errors and the mean relative errors (in brackets) estimated for the permeate mass fluxes of water were 16.2% (8.4%), and 6.7% (3.8%), and for the permeate mass fluxes of ethanol were 54.6% (18%), and 33.7% (13.6%) for the PERVAP™ 4100 and 4100 H F, respectively. The results presented in Fig. 8 (a, b) and 9 (a, b) are similar to those shown in Fig. 6 (a, b) and 7 (a, b). The highest and the mean (in brackets) relative errors estimated for the IPA-water-PVA system are as follows: 10% (5%) and 5.8% (2.8%) for the permeate mass fluxes of water and 36% (14.4%), and 29.1% (12.6%) for the permeate mass fluxes of IPA for the PERVAP™ 4100 and 4100 H F, respectively.

The highest deviations occurred at low feed water concentrations for the permeation flux of ethanol and isopropanol, where the theoretical values roughly fit with the experimental data for both membranes. These deviations are attributed to the dryness of the membrane at a low water concentration in the feed and the low feed temperature that leads to a low permeation flux; this means that collecting the permeate sample requires a long time, which may affect the accuracy of the permeation flux measurement of ethanol and isopropanol.

Statistical performance parameter (Relative error) is used to evaluate the closeness between the permeation flux model predicted and the experimental data using Eq. (38). Relative error (RE) is defined as the ratio of the size of absolute error (the difference between a measured value and a true value) to the size of the true value. RE has been expressed in percentage by multiplying it by 100 and has

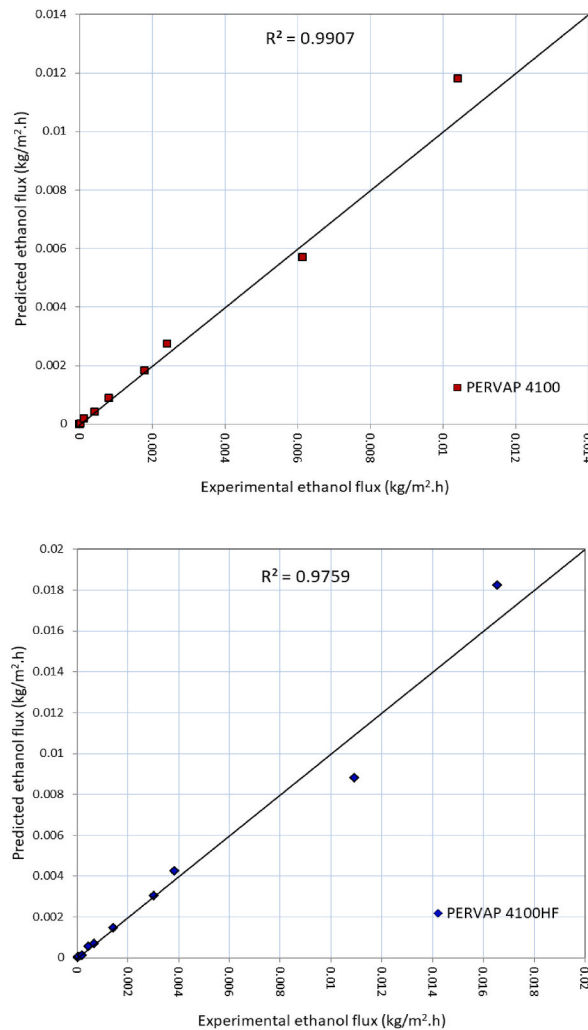


Fig. 7. Comparison of the experimental and predicted mass fluxes of ethanol (kg/m²h) in the ethanol-water systems for the a) PERVAP™ 4100 and b) PERVAP™ 4100 H F membranes.

no units [55].

$$\text{Relative Error} = \frac{|\text{True Value} - \text{Measured Value}|}{\text{True Value}} = \frac{|J_{i,exp} - J_{i,theory}|}{J_{i,exp}} \tag{38}$$

The comparison between the experimental and modeled data are presented in the Supplementary Material (Tables 1S, 2S, 3S and 4S) for alcohol-water systems in a range of feed compositions at 60, 65, and 70 °C.

Furthermore, the degree of closeness between the predicted permeation flux and the experimental data were evaluated using statistical performance parameters, such as the coefficient of determination (R²) and relative root mean square error (RMSE), with the results presented in Table 3.

The coefficient of determination (R²) was estimated using Eq. (39) to evaluate how accurately the theoretical regression line approaches the experimental results. The R² ranges between 0 and 1, with a value higher than 0.9 indicating a very good regression model [56].

$$R^2 = 1 - \frac{\sum_{i=1}^N (J_{i,exp} - J_{i,theory})^2}{\sum_{i=1}^N (\bar{J}_{exp} - J_{i,exp})^2} \tag{39}$$

The root mean square error (RMSE) was estimated using Eq. (40), where a smaller value of the RMSE indicates a better fit between the predicted mass flux and the experimental data [57].

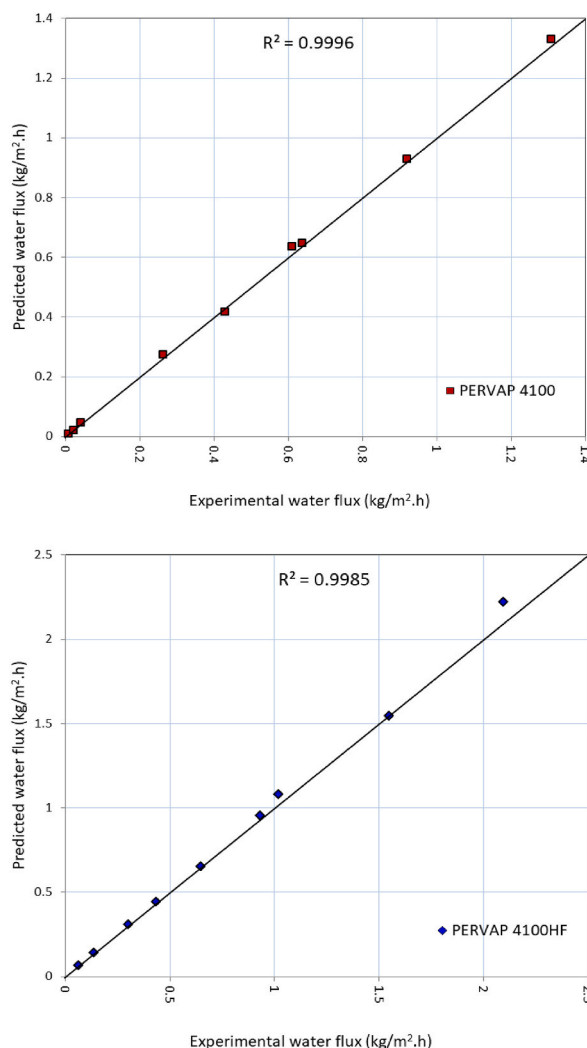


Fig. 8. Comparison of the experimental and predicted mass fluxes of water (kg/m²h) in the IPA-water systems for the a) PERVAP™ 4100 and b) PERVAP™ 4100 H F membranes.

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (J_{i,exp} - J_{i,theory})^2} \tag{40}$$

As shown in Table 3, the R² values for water and alcohol fluxes were high, while the RMSE values were low, which means that the correlation between the experiments and the model prediction was good for both water and alcohol in ethanol-water systems and isopropanol-water systems.

9. Conclusions

Alcohol-water-PVA membrane systems form a highly nonideal mixture. The transport of alcohol and water across commercial PVA membranes was simulated using the UNIQUAC model to describe the sorption of alcohol-water mixtures in membranes and to predict the activity of nonideal mixtures (alcohol-water) in the PVA polymer matrix. A model was proposed that combines the UNIQUAC model and the fundamental transport equation of solution-diffusion theory. The PV experimental data with the developed mass transport model was used to predict the diffusivity correlations for water and alcohol (i.e., ethanol and isopropanol) across the PVA membranes. It was found that the diffusivity of water and alcohol through the PVA membrane increases exponentially with the activity of the feed water and that the water diffusivity is higher than the ethanol and isopropanol diffusivity. Also, it was observed that for swollen membranes (PVA), the developed correlations of water and alcohol diffusivity were strongly influenced by the feed water activity and feed temperature. The mass transport model with developed diffusivity correlations was used to predict the performance of membrane (the permeation flux of water and alcohol across the PVA membranes), and the results showed a good agreement between

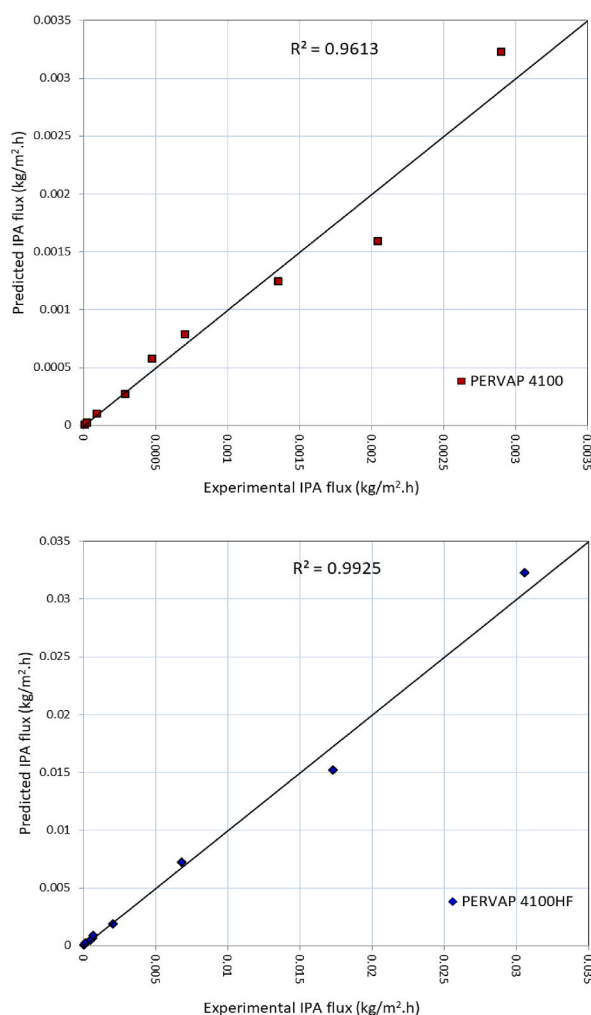


Fig. 9. Comparison of the experimental and predicted mass fluxes of IPA (kg/m²h) in the IPA-water systems for the a) PERVAP™ 4100 and b) PERVAP™ 4100 H F membranes.

Table 3

Accuracy of the water and alcohol partial fluxes between the experimental data and the theoretical model.

Membrane	Ethanol-water mixture				IPA-water mixture			
	Water		Ethanol		Water		IPA	
	R ²	RMSE	R ²	RMSE	R ²	RMSE	R ²	RMSE
PERVAP™ 4100	0.9907	0.01952	0.9789	0.00047	0.9593	0.01329	0.9990	0.00019
PERVAP™ 4100 H F	0.9965	0.01749	0.9737	0.00085	0.9947	0.04636	0.9918	0.00090

the experimental data and the predictive model. The highest relative errors and the mean relative errors (in brackets) estimated for the permeate mass fluxes of water were 16.2% (8.4%), and 6.7% (3.8%), and for the permeate mass fluxes of ethanol were 54.6% (18%), and 33.7% (13.6%) for the PERVAP™ 4100 and 4100 H F, respectively, as well as for the IPA-water-PVA system are as follows: 10% (5%) and 5.8% (2.8%) for the permeate mass fluxes of water and 36% (14.4%), and 29.1% (12.6%) for the permeate mass fluxes of IPA for the PERVAP™ 4100 and 4100 H F, respectively.

Author contribution statement

Nada Mahdi Farhan: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Salah S. Ibrahim, Qusay F. Alsahy: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed

reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supp. Material/referenced in article.

Declaration of interest's statement

The authors declare no competing interests.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e13713>.

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